POLAROGRAPHY OF SOME ORGANIC COMPOUNDS AT THE ROTATING MICROANODE

By

Oscar C. Bridgeman, Jr.

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Harvard College

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THESIS AND ABSTRACT APPROVED:

Paul Arthur
Thesis Adviser

O C Dermer
Faculty Representative

W. E. McTurlough
Dean of the Graduate School

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HISTORICAL

The polarographic technique of electrochemical analysis was developed about 30 years ago by Professor Jaroslav Heyrovsky at Charles University, Prague, Czechoslovakia. The polarographic method involves the interpretation of a plot of current versus the applied potential as obtained when a compound in solution is reduced or oxidized at a small polarizable electrode. Although the first work was done on a manual apparatus and the curve plotted by hand, in 1925 Heyrovsky and Shikata[7] developed an instrument for plotting the curve automatically. This instrument they named the polarograph, while the curves so obtained they called polarograms.

The ideal type of polarogram is illustrated in Figure 1. The "half-wave potential" ($E_{1/2}$) is found to be characteristic of the substance being reduced or oxidized. The diffusion current (I_d) is, in most cases, proportional to the concentration of the reacting substance. Using these relationships, it is possible in some cases to qualitatively and quantitatively analyze a solution for as many as four or five ions or compounds in one determination.

In the most general terms, a polarogram is obtained by plotting the current versus the applied potential as the latter is steadily increased across an electrolysis cell consisting of a small, easily polarizable electrode (hereafter referred to as the microelectrode) and a large non-polarizable electrode (called the reference electrode). The reference electrode maintains a constant value throughout the electrolysis, so that the reaction at the microelectrode is the reaction being measured.

A solution that is to be analyzed polarographically usually consists of three components; (1) the solvent, (2) the reducible or oxidizable material, and (3) the carrier electrolyte. The solvent may be water, a

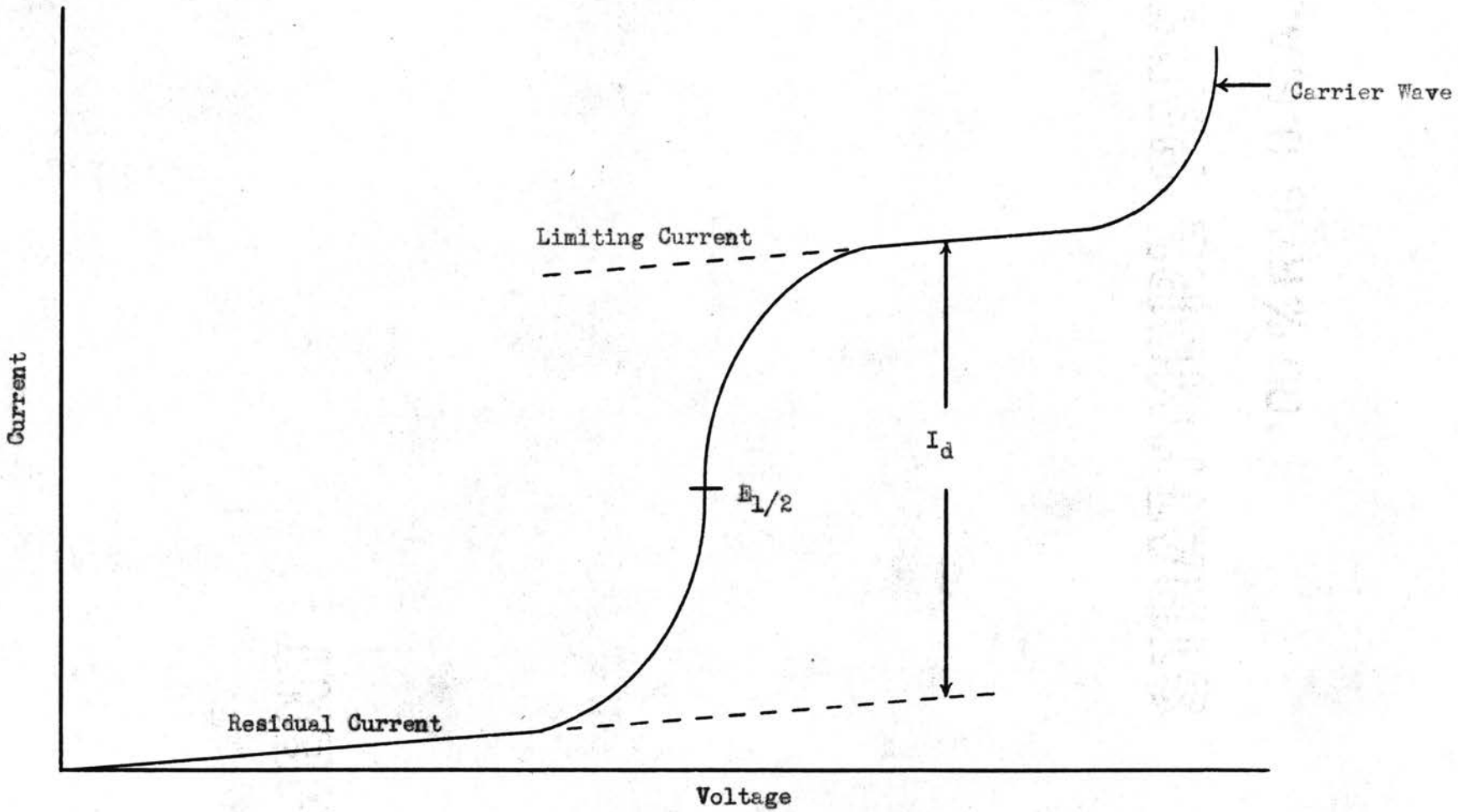

Figure 1

Ideal Polarographic Wave

solution of water and some organic solvent, such as methanol or ethanol, or in some cases an entirely non-aqueous solvent, such as acetone. For polarographic analysis the reducible or oxidizable material to be measured is found in concentrations of 10^{-2} to 10^{-6} molar. There are some isolated cases where higher or lower concentrations have been used. The carrier electrolyte is some ionizable substance which acts in the capacity of the carrier of the current. It is desirable that this carrier electrolyte be from 50 to 100 times as concentrated as the reacting substance. The function of the carrier electrolyte is to minimize the electrical migration of the reacting substance to the electrode, thus insuring that the diffusion current is really due to the diffusion of the substance to the electrode surface. Should the reacting substance have the same ionic mobility as the carrier electrolyte, a carrier electrolyte of 100 times the concentration of the reacting substance would carry approximately 99 percent of the current. This would make the assumption of a negligible electrical migration of the reacting substance within the experimental error.

There are three types of microelectrodes in common use today. The first electrode developed, and the most generally used, is the dropping mercury electrode (D.M.E.). The dropping mercury electrode consists of a mercury reservoir arranged to maintain a constant head of mercury, connected to a piece of very fine capillary tubing. Suitable capillary tubing is available from the Corning Glass Works under the name of "marine barometer tubing". Pieces of this tubing can be chosen to have a uniform bore of the order of 0.05 mm. in which case a length of 5 to 30 cm. will give the desired flow rate of a drop every 3 to 6 seconds. Ilkovic[9] developed the classical equation named after him, relating the diffusion current at the D. M. E. with the other variables in the reaction. The Ilkovic equation states:

$$i_d = 605\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}$$

where

i_d = current in microamperes

n = number of electrons involved in electrode reaction

D = diffusion coefficient of substance reacting expressed as $cm.^2$ $sec.^{-1}$

C = concentration in millimoles per liter

m = weight of mercury flowing in milligrams per second

t = drop time in seconds

For any given reaction at any particular capillary in a given environment all these terms except i_d and C are constants; consequently, this equation gives the relationship that the diffusion current is proportional to concentration. This equation holds only for reversible reactions at the D. M. E. Some modifications of the Ilkovic equation have been made recently. The weakness of the Ilkovic equation lies in the fact that the curvature of the surface of the mercury droplet has been neglected. Taking into account the curvature of the droplet, Lingane and Loveridge[22] and Strehlow and von Stackelberg[35] have independently derived the relationship:

$$i_d = 607\ n\ D^{1/2}\ C\ m^{2/3} t^{1/6} \left(1 + \frac{AD^{1/2}t^{1/6}}{m^{1/3}}\right)$$

where A is a constant and the other terms have the same meaning as in the original equation. Lingane and Loveridge found A to be 39 at 25°, and Strehlow and von Stackelberg found it to be 17. Lingane and Loveridge[22] also found that the original Ilkovic equation could be used if the exponent of 2/3 on the quantity m was replaced by 0.64.

Although the D. M. E. is extremely useful in cathodic studies, its use anodically is limited. The major problem in trying to use the D. M. E. in

anodic work is that mercury itself is oxidized at about +0.4 v. (versus the saturated calomel electrode), undergoing the reaction:

$$2Hg \longrightarrow Hg_2^{++} + 2e$$

The potential of this reaction is dependent on the medium, but +0.4 v. is near the maximum positive potential that can be obtained with the D. M. E.

A second type of microelectrode that has had some use in polarography is the stationary platinum electrode. This electrode has a much greater range in anodic work than does the D. M. E., for the electrode material is relatively inert. However, the electrode does have the disadvantage of necessitating a one-to two-minute wait for equilibrium to be attained for each potential advance, an exceedingly slow rate of increasing the voltage with an automatic instrument (as has been used in some cases[10,31,32]), or the use of high temperatures to increase the speed of attainment of complete concentration polarization, as in the work of Skobets, Torov, and Ryabokon[33]. Müller[25] has reported developing an apparatus using the stationary platinum electrode, where the electrolyte solution flows past the electrode at a uniform rate. This apparatus is suitable for use with automatic recording polarographs but is very sensitive to changes in the rate of flow of the solution.

Using Fick's First Law[4], Kolthoff and Lingane[15] derived the following equation relating i_d to concentration:

$$i_d = knDC$$

where

n = number of electrons in reaction

D = diffusion coefficient of the reacting substance in $cm.^2\ sec.^{-1}$

C = millimolar concentration of reacting substance

They were able to prove experimentally the accuracy of this relationship for several ions tested.

The third common type of microelectrode, and the one used in this research problem, is the rotating platinum microelectrode. This electrode is usually 0.5 mm. wire projecting about 3 mm. from the side of a shaft coated with an insulating material and rotated in the solution at about 600 r.p.m Laitinen and Kolthoff[19] have found that there is no increase in diffusion current at speeds of rotation greater than 600 r.p.m. They also noted that using the same solutions with the rotating electrode as those used on a stationary platinum electrode the same size, they observed about 20 times the diffusion current found with the stationary electrode. It is doubtful if the rotating electrode ever reaches equilibrium with the solution, but it maintains the same percentage of the equilibrium current at all times.

Randles[30] has done a graphical solution to a rotating microelectrode, but in his derivation he imposed three conditions which make the resulting equation not applicable to this work. These conditions are that: (1) the rotated electrode be spherical in shape; (2) the reaction at the electrode be reversible; and (3) the product be soluble in the solution. It is believed that none of these conditions apply to the work reported here.

The anodic branch of polarography has received little attention compared to the large amount of work that has been done at the cathode. As in cathodic work, most anodic work to date has been done at the D. M. E. There have been several inorganic ions oxidized at the D. M. E. in recent years. Struble[36] reports that the titanous ion gives an anodic wave in dilute HCl, while Verdier[37] has oxidized manganous tartrate. More recent work is that of Lingane and Meites[23] on the oxidation of V^{+4}. There are a number of reversible organic reactions that have been studied. The cystine-cysteine system, both anodic and cathodic, is the subject of a chapter in Kolthoff and Lingane[15]. Kolthoff and Barnum[12] also report results on cysteine at the platinum electrode, using perchloric acid as the carrier electrolyte. Several oxidation-reduction

potentials have been studied at the D. M. E., including the work of Müller and Baumberger[28] on the quinone-hydroquinone system, and followed by further work by Müller[27] on quinhydrone. Müller[26] also determined the potential of α-hydroxyphenazine. The oxidation potential of the chromocyanide-chromicyanide system was studied by Hume and Kolthoff[8]. More unusual types of reactions are the ones studied by Smith, Kolthoff, Wawzonek and Rouff[34] on the oxidation of the hydroxy-chromans and hydroxycoumarans. In this case the electrode reaction is reversible, but since the reaction products are unstable, the overall reaction is irreversible.

There is another type of anodic reaction that we should consider at the dropping mercury electrode. Kolthoff and Miller[16] have found that ions which form insoluble or very slightly ionized salts with mercurous ion will tend to decrease the positive potential of the mercury oxidation, and do so in a manner characteristic of the ion. Therefore ions of this type give waves, and may be analyzed. This was done on Cl^-, Br^-, I^-, $S^=$, $S_2O_3^=$, CN^-, CNS^- and OH^-.

There is also to be considered the irreversible type of reaction at the D. M. E. The first of these to be reported was the oxidation of ascorbic acid by Kodicek and Wenig[11]. Skobets and Atamanenko[31,32] ran ascorbic acid at the stationary platinum anode, and found a sharply defined wave. Vlcek, etal.,[38] oxidized catechol in phosphate buffers, but found some interference from the reaction of phosphate ion with mercury. Doskocil[3] repeated this work in acetate buffer solutions with good results, and also got waves from 4-methyl-o-benzoquinone, β-naphthoquinone, and pyrogallol. Lester and Greenberg[20] report the oxidation of phenylhydroxylamine at the D. M. E. Some recent articles on other organic compounds report the oxidation of sodium diethyldithiocarbamate by Gregg and Tyler[6], and the anodic reaction of thioglycolic acid by Liberti and Cervone[21]. The continuation of this type of work unfortunately is limited

by the low oxidation potential required to oxidize the mercury itself. These are just the few cases of compounds which have been found to give anodic waves below the oxidation potential of mercury in the particular carrier solution used.

There has been some anodic work at the stationary platinum microelectrode where there is not the potential limitation of the D. M. E. However, the electrode is rather tedious to use, due to the fact that it must be allowed to reach equilibrium at each potential setting—a matter of one to two minutes. Laitinen and Kolthoff[18] found that this technique gave good results. Glasstone[5] first used this electrode for polarographic purposes, and found the diffusion current proportional to concentration in the oxidation of ferrocyanide ion, ferrous ion, hydroquinone, and hydroxylamine. Skobets and Atamanenko[31,32] oxidized pyrocatechol and ascorbic acid to give well defined waves, but resorcinol, oxalic acid, ethanol and formic acid gave curves with sharp maximum peaks, which they did not attempt to explain. Walen and Haissinsky[39] also oxidized oxalic acid, in addition to reporting the formation of a wave in the anodic deposition of PbO_2. Julian and Ruby[10] have used the stationary platinum microelectrode to determine the half wave potentials of several organic compounds. By using an apparatus which increased the potential at a rate of 10 to 20 millivolts per minute they were able to use an automatic recording device. Between runs they cleaned the platinum electrode with concentrated HNO_3, washed with distilled water, then with chromic acid, then again with distilled water. They investigated several phenylenediamines and p-aminophenol.

The electrode used for the research reported here was the rotating platinum electrode. It has the advantages of being easily used with the automatically recording polarograph. It also gives a considerably larger diffusion current than the stationary platinum electrode. Nernst and Merriam[29] were the first to use a rotating Pt electrode, before the days of

polarography. Kolthoff and Harris[13] have used the electrode in amperometric titrations. Laitinen and Kolthoff[19] oxidized ferrocyanide at the rotating electrode using KCl as the carrier electrolyte, but in order to obtain reproducible results they found it necessary to evolve oxygen from the electrode for a few minutes before each determination. Delahay and Stiehl[2] have reported the oxidation of thallous ion at the rotating electrode. Between runs they rinsed the electrode with concentrated H_2SO_4 to remove the product, $Tl(OH)_3$. Kolthoff and Jordan[14] also oxidized thallous ion at the rotating platinum electrode, storing their electrode in 10M HNO_3 between runs in order to obtain reproducible results. MacNevin and Sweet[24] have recently reported that they obtained current versus voltage curves for methanol and ethanol at a platinized rotating platinum electrode.

One other work of note in the field of anodic polarography is the work of Bortmes[1]. Using primarily the rotating platinum electrode, but occasionally a gold electrode, he was able to obtain good waves for iodide, sulfite, and stannous ions. Reproducible waves were obtained for iodide without treating the electrode when the runs were made in 0.36 N H_2SO_4 and the maximum voltage was limited to +1.0 volts vs. the S. C. E. For the other ions, various treatments were required for the electrode between runs. These will be discussed later in connection with the studies covered in the present research. In contrast with the results reported by Laitinen and Kolthoff[19], Bortmes[1] found that freshly prepared solutions of ferrocyanide gave good waves when 0.1N sodium sulfate was used as the carrier electrolyte and when a freshly-scraped electrode was used, but gave poor results if the anode was first polarized.

PURPOSE OF RESEARCH

The purpose of this research is threefold. Since there has been so little anodic polarography of organic compounds, it was felt that it would be of interest to investigate to what classes of compounds this method of analysis might be applicable. After this preliminary investigation, an extensive study was to be made on one or more compounds. From the results of all these experiments it was hoped that we would be able to obtain information on the factors influencing the results in this type of polarography. It was known from Bortmes[1] work that the factor of greatest interest would probably be the polarization effect that makes necessary the pretreatment of the electrode before each determination in order to get reproducible results. A general solution to this problem, including a general treatment for all cases, was one of the major aims of the investigation.

EXPERIMENTAL

Apparatus

Two polarographs were used in this research, the preliminary investigations being made on a Sargent Model XXI recording polarograph while the later stages of work were done on an instrument of our own construction. In the latter instrument, the automatic bridge and photographic recording unit were parts from a Sargent Model XII instrument. The galvanometer was a special one of the type used in the Model XII but having a sensitivity of 0.0047 microamperes per scale division, a period of 3.5 seconds, an internal resistance of 200 ohms and a critical damping resistance of 2200 ohms. This instrument was equipped with a chain of gears providing a variable speed drive, so that the full span range, from 0 to 1.0 on the camera scale, could be transversed in a time that could be varied from 30 seconds up to 5 hours. It also had a preset voltage circuit similar to that on the Sargent Model XXI. In addition to these features, a Brown Recording potentiometer (Model No. 153x12V-X-30) having a 10 millivolt full-scale sensitivity and a pen speed of 4.5 seconds was attached to the instrument, so that either visual or photographic records could be made.

The electrode was of conventional design (Figure 2). A platinum or gold wire was mounted in a steel shaft 12 mm. in diameter. This shaft, mounted in a brass bearing, was driven by a 1/20 h.p. rubber-mounted motor, the motor and shaft being connected by pulleys and a drive belt which served to reduce the speed of the shaft to 600 r.p.m. The shaft was coated with ceresin wax and the electrode scraped clean. The electrode thus exposed was about 0.5 mm. in diameter and 3 mm. long. To insure that, in scraping, a reproducible surface area was bared and to prevent injury to the wax insulation, a soft-glass bead about 2.5 mm. in diameter was fused onto the electrode

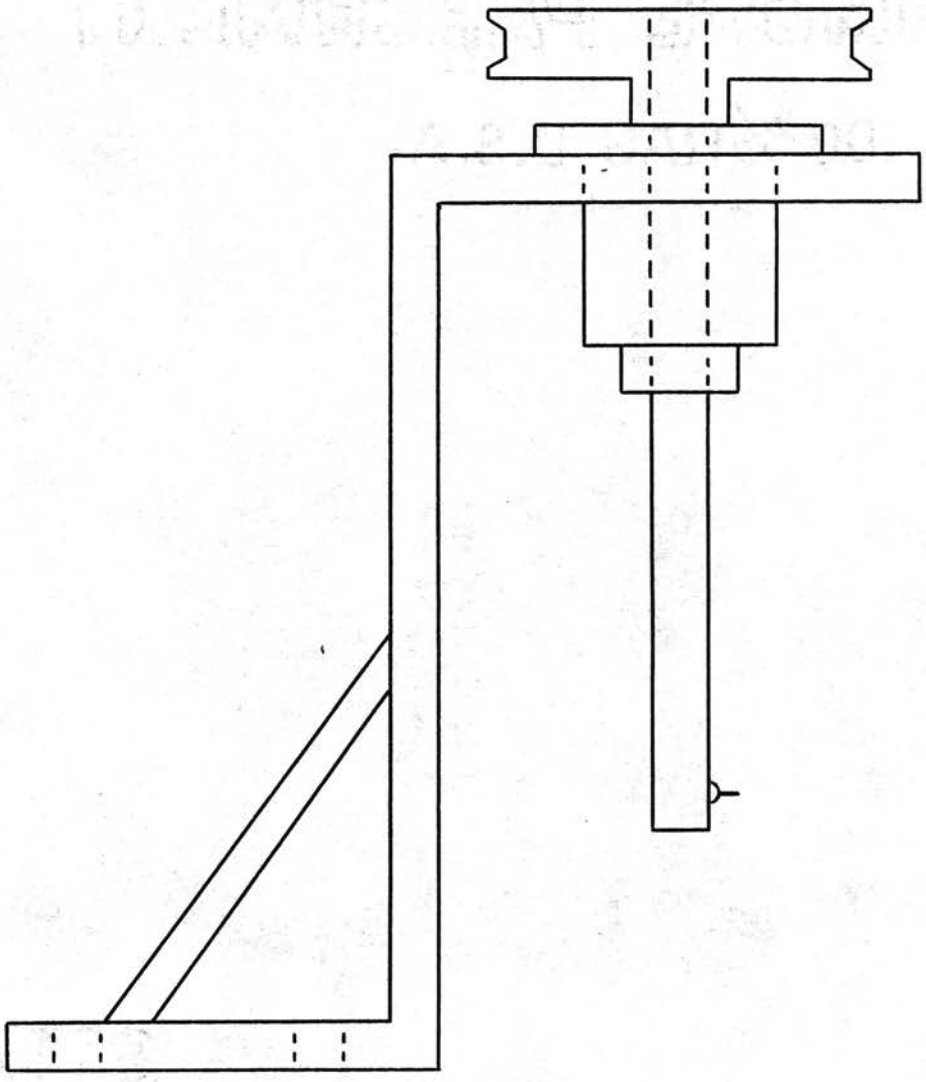

Figure 2

Electrode Assembly

wire near its base, and the electrode and bead were soldered in place in the shaft by Wood's Metal. The glass bead was set to protrude about half way out of the shaft and, in scraping the electrode, care was taken to scrape to the glass surface each time. Considerable difficulties were encountered in sealing a glass bead to gold wire, but by use of a microburner and great care it was found to be possible. It is relatively easy to form such a bead on platinum when a small hot flame such as that produced by a small gas-oxygen torch is used.

The cell employed was of the H-cell type (Figure 3), with a sintered glass disk and glass wool packing in the connecting arm to limit diffusion. The two halves were connected by a ground-glass ball and socket joint. To reduce resistance in the cell, the connecting arm was made of fairly large bore (about 7 mm. I. D.) tubing. With this arrangement and with the solutions employed, the cell resistance was found to be of the order of 1000 ohms. Agar was not used in the liquid junction, for it was found that in alkaline solution (0.1N NaOH) spurious waves showed up occasionally, and evidence indicated that these irregularities could be due, in part, to the agar. Agar dissolved in an alkaline carrier electrolyte was found to give an anodic wave of sorts.

All measurements were made with the cell inserted in a constant temperature bath which was connected to a central system supplying water at $25.0 \pm 0.1°C$.

Three reference electrodes were used during the course of the problem. An attempt was made to use the mercury pool during the preliminary investigations. However, since in this work the reference electrode was to function as the cathode, it was soon realized that, except at high voltages, no reaction could take place at this electrode, and any current flowing would be subject to control by both electrodes rather than by the micro electrode alone. The

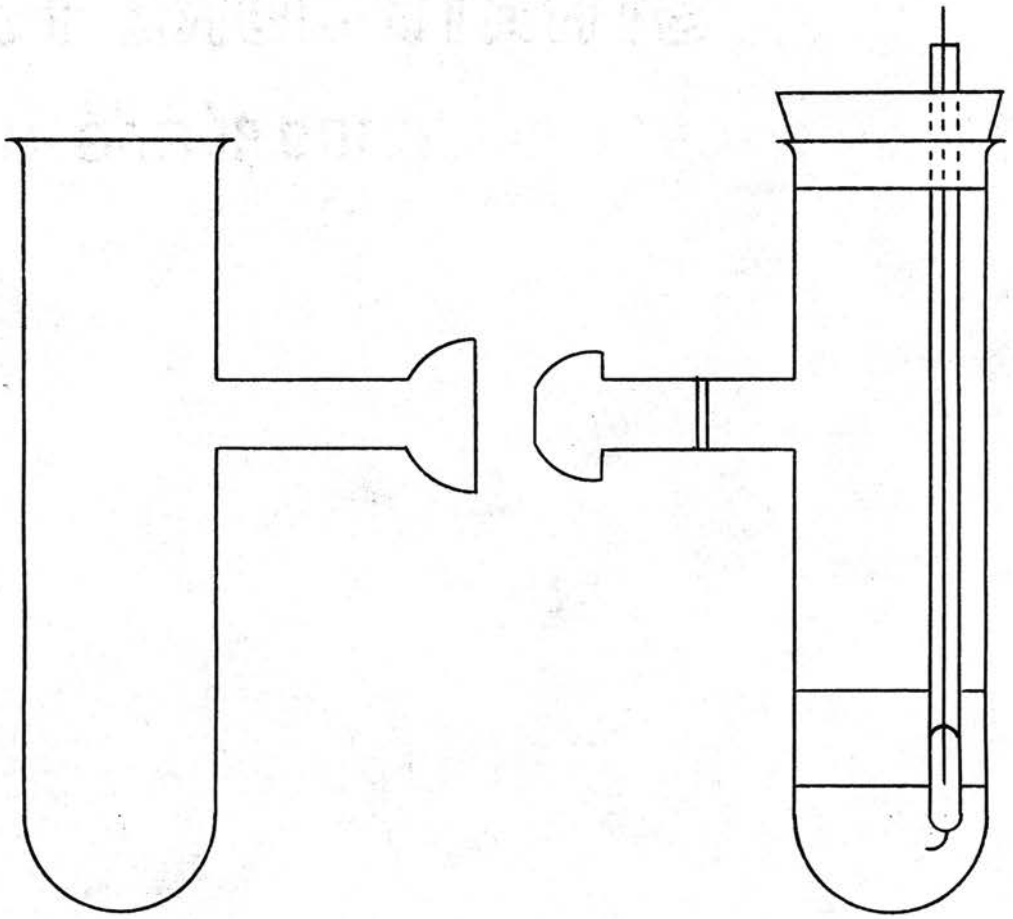

Figure 5

Reaction and Reference Cells

A-Reaction cell

B-Mercurous sulfate reference cell

next reference cell tried was the saturated calomel electrode (S. C. E.). As a reference the S. C. E. gave excellent results, but it was found that small amounts of chloride ion diffusing through the salt bridge from the reference electrode caused trouble with the determinations. Since this was the case, it seemed advisable to use another electrode, and the mercury-mercurous sulfate electrode was decided on. This electrode was made up to be saturated with K_2SO_4 and it was found that sulfate ions diffusing through from this electrode did not cause trouble. Several runs were made interchanging the two reference electrodes, and if a preset of 0.3 volts opposed was used with the mercury-mercurous sulfate electrode, the results obtained with the S. C. E., but without the chloride interference, could be closely approximated by applying a further correction of 0.1 volt.

Since any oxygen in the solution to be analyzed might react with, and reduce the concentration of oxidizable substances, each solution was degassed for 30 minutes before the run was made and nitrogen was passed over the surface of the solution while the polarogram was being made. The nitrogen used was water-pumped nitrogen supplied by the Linde Co., and before use was passed through a train consisting of concentrated sulfuric acid, alkaline pyrogallol, and distilled water.

All reagents used were either C. P. or reagent grade, and were used directly from freshly-opened containers. The only reagent purified further was the potassium hydrogen phosphate used in the buffer solutions, in which case the C. P. product was recrystallized twice from distilled water.

Some exploratory work was done originally employing 0.1N NaOH, 0.1N KCl, and 0.1N HCl as carrier electrolytes. Since it was expected that the reactions to be studied would be pH sensitive, therefore requiring a buffer solution, and since it was learned early that chloride ion interfered with the determinations, it was deemed advisable to use as carriers a series of buffer

TABLE 1

Phosphate Buffer Solutions*

pH	Milliliters of 0.200N				pH of Calibration Solution
	NaOH	KH_2PO_4	H_2SO_4	K_2SO_4	
3.00		45.00	4.32	17.0	2.80
5.00	0.58	49.00		12.3	4.80
7.00	16.65	27.00		6.7	7.00
9.00	20.57	20.00		7.3	9.00
10.00	24.25	23.50		0	10.20
11.00	25.77	23.00		0.3	10.80

*These proportions are on the basis of 100 ml. of buffer solution, the volume being brought up to this magnitude with distilled water. The potassium sulfate was added to bring the solutions up to an ionic strength of 0.142.

solutions not containing any chloride ion (see Table I). The original solutions were made up and checked with the Beckman Model H pH meter. Standard pH's for calibrations were obtained using Coleman buffer tablets. Since it was desired to make all determinations at the same ionic strength, all buffer solutions were brought up to an ionic strength of 0.142 before the determinations were made. A 0.2N solution of K_2SO_4 was used for this purpose. Each buffer solution was believed accurate to its listed pH $\pm$ 0.05 units.

For the photographic determinations, the paper used was Eastman Kodak Kodabromide paper, F-1 speed. It was found necessary to sensitize the paper for the high-speed runs by pre-exposing it for 1 or 2 seconds to the diffuse light from a 25 watt bulb, at a distance of 12 feet.

Depolarization of the Electrode

This section deals with the electrode pretreatments tried in an effort to make the electrode behave in a reproducible manner. The term polarization has been applied to any electrode effect that tends to inhibit the passage of current. It is in that sense that the term is used here, the term being used to covery any effect produced by electrolysis that prevents the repeated use of an electrode without preliminary treatment. There is justification for the belief that, in the work done with the platinum microelectrode, this polarization effect is caused by the formation of reaction product on the surface of the electrode, this being true even if only a carrier electrolyte is used. It has been found by Bortmes[1] and also by this investigator that the types of polarization present, and therefore the depolarization treatments needed, vary with both the carrier electrolyte and the oxidizable substance being determined. For example, Bortmes[1] found that in the determination of iodide, if he used a 0.36N sulfuric acid solution as the carrier electrolyte

no polarization occurred, the carrier itself apparently acting as the depolarizing agent. In other cases, however, it was necessary to wash the electrode with concentrated sulfuric acid. In some cases he found that reversing the polarity of the electrode for a few minutes in order to reduce the oxidation product gave acceptable results.

Polarization seems to give rise to two difficulties. In the first place, if successive runs are made without depolarizing the electrode, each succeeding run becomes much weaker and less reproducible than the preceding one---as if the polarization is building up. The second important effect of polarization is the distortion of the original polarographic wave. The wave rises as if to follow a normal polarographic curve, but reaches a maximum and then rapidly drops off, leaving a peak in the curve. Both of these phenomena indicated that some change was taking place at the electrode surface; consequently, the depolarization techniques tried were directed toward the removal of possible oxidation products and the reconditioning of the electrode surface.

The various depolarization techniques tested will be discussed in detail with respect to the type of electrode used, i. e., platinum or gold. The major part of this study was made with the platinum electrode, so that will be considered first.

Reversing Current In Reaction Solution. This technique which was used by Bortmes[1] in some cases, was tried on several solutions at various times. The procedure was to reverse the polarity of the polarographic cell, making the platinum electrode the cathode at a potential of -1.2 v. with respect to the S. C. E. This was done for periods of time from 30 seconds to several minutes. In both 0.1N NaOH and 0.1N HCl the electrode was apparently depolarized enough to show waves, but in the acid medium the depolarization seemed erratic. It appeared first that the method would be successful in alkali,

but soon it was noticed that a hump usually appeared in the curve after depolarizing in this manner. This hump occurred at about +0.5 volts vs. the S. C. E. In order to see if this hump was possibly due to formation of peroxide at the electrode, a solution of H_2O_2 was run, the concentration being about 10^{-2} molar. No wave was found, and further concentration increases did not develop a wave.

Concentrated Sulfuric Acid. Washing with concentrated sulfuric acid was tried briefly, but this treatment did not appear to be as useful as it was in the work of Bortmes[1]. It appeared to give fairly reproducible results, with a slight wave on the carrier curve just before it went off the scale. However, when this technique was used a wave which had appeared for acetaldehyde in another instance failed to show up; consequently, it was assumed that a good cleaning of the electrode was not being accomplished. Similar results were obtained with 18N H_2SO_4.

Distilled Water Wash. This was tried on several occasions, but the material on the electrode did not seem to be affected. The electrode surface was not clean and shiny and poor results were obtained.

Dilute Sulfuric Acid Wash. This gave the same effect as the other acid washes, but in addition, the current would often jump off the scale at the first small increase in potential at the beginning of the electrolysis.

Titanous Chloride Wash. It was felt that a moderately strong reducing agent might clean the electrode after an oxidation. Titanous chloride was tried for this purpose, but the results obtained were quite erratic. Since such erratic behavior was always observed when the electrode came in contact with chlorides, and since the $TiCl_3$ had to be kept in a strong HCl solution, it was believed that at least some of the difficulty was due to the chloride present and possibly adsorbed onto the electrode surface.

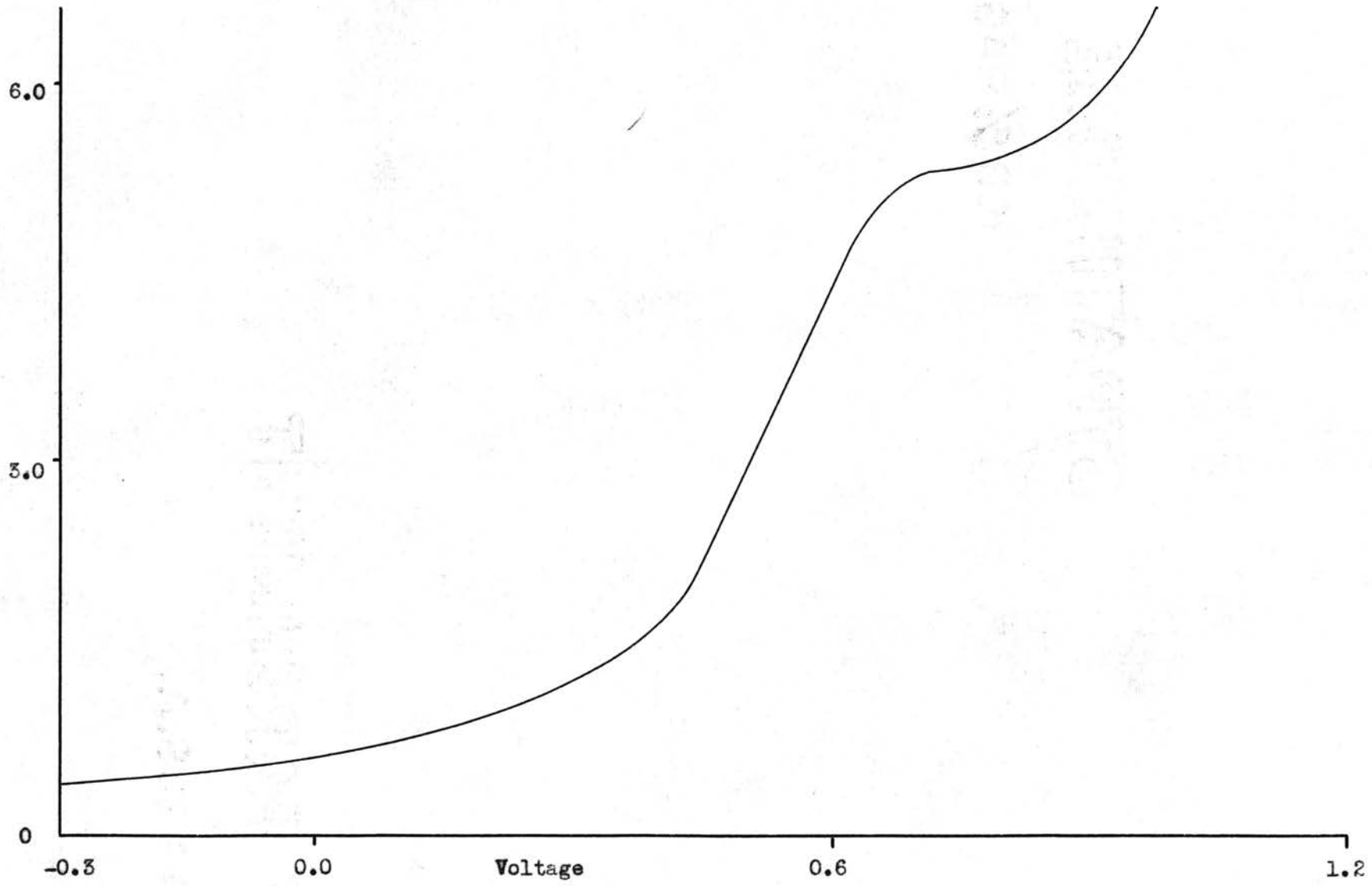

Figure 4

Carrier Wave after Depolarization by Hydrogen Evolution, Scan Speed 100 Millivolts per Second (Reference electrode, sat. $Hg|Hg_2SO_4$.)

Hydrogen Evolution. The next technique applied in an attempt to condition the electrode involved the electrolytic evolution of hydrogen from the surface of the electrode. As a current source two cells of an ordinary storage battery were used. Since it was realized that some of the hydrogen would be adsorbed at the platinum surface, it was decided to wash the electrode after the evolution with a dilute solution of iodine. The hydrogen was evolved from a 1N sulfuric acid solution. On the first attempt hydrogen was evolved from the electrode for 30 sec., the electrode then being washed with distilled water. The electrode was then treated with iodine solution for 15 seconds, then rinsed with distilled water again. This procedure seemed to give excellent results and, due to the reduction of possible oxidation products by hydrogen or to the mechanical loosening by the bubbles, or both, the electrode surface was clean and shiny and gave good waves with phenol. Unfortunately, after several treatments of the electrode with hydrogen a secondary wave appeared, even in the case of the carrier electrolyte solution which contained no oxidizable material. The wave was a well-formed, sharply defined one with a half-wave potential of about +0.62 vs. the S. C. E. It was thought that possibly we could eliminate this wave by washing the electrode longer with iodine, but washes up to one minute did not decrease it noticeably. Other washes were tried, including one with 3 percent H_2O_2. In other cases, oxygen was evolved at the electrode surface for 30 seconds after hydrogen generation for 5 minutes; then the electrode was washed in an acid solution of ferrous ammonium sulfate to remove the adsorbed O_2 from the electrode. In all of these, however, the wave persisted and could be removed only by unusually vigorous scraping of the electrode surface. Figure 4 gives a picture of this wave, run at a 30-second span time. Table 4 gives the measurements taken on this wave in

an attempt to determine the number of electrons involved in whatever reaction was responsible for the wave.

Since the wave obtained when hydrogen evolution was used occurred in the range of some of the waves studied in this research, it was necessary to abandon this method of depolarization in spite of the otherwise desirability of the combined reducing and mechanical washing action of the evolved hydrogen.

Scraping the Electrode. The technique of scraping the platinum electrode between determinations was the method finally adopted in this research. It has the advantage of guaranteeing a clean surface for each run if the scraping is thoroughly done. It has the obvious disadvantage of being very tedious, and over a period of time it will cause a change in the area of the electrode surface exposed to the reaction. This technique does give reproducible results and was found to work very well. A sharp razor blade was used, and care was made always to scrape back to the glass bead in which the electrode was seated. It was this technique that enabled the successful work on the determination of phenol to be done.

In treating the gold electrode for polarization some of the same techniques tried on the platinum electrode were used. It was noted that the gold electrode did not seem to be as easily polarized in the carrier solution as was the platinum and a similar phenomenon was frequently observed in solutions of compounds being investigated. On the other hand it was noted that when the gold electrode did become polarized it was more difficult to depolarize than in the case of the platinum electrode. Due to the much greater softness of gold it was difficult to use the scraping technique without seriously damaging the electrode; consequently, this solution to the problem was not satisfactory. Several other techniques were tried.

Reversing Current Between Runs. This seemed to give results similar to those obtained with the platinum, the characteristic hump being present after a few runs. This method of depolarization was abandoned when it was found that phenol, which worked well with platinum, gave no wave at the gold electrode even when concentrations as great as 0.1 molar phenol were used.

Concentrated Sulfuric Acid Wash. This method was entirely unsatisfactory with the gold electrode. Erratic waves invariably were obtained even in the carrier solution alone.

Hydrogen Evolution. This method, which had been tried with platinum, was also tried at the gold electrode, with entirely similar results except that the wave came at a slightly different potential. The half-wave potential in this case was +0.70 vs. the S. C. E.

At this point it seemed that platinum electrodes were giving the best results; consequently, the rest of the work was done using platinum for the electrode.

Results and Discussion

In the early part of this work a number of organic substances were tested in an effort to determine (1) conditions necessary to obtain good anodic waves and (2) the classes of organic compounds likely to yield such waves. Unfortunately, most of these compounds were studied using the S. C. E. as reference electrode and before it was realized that chloride ions diffusing into the solution from the S. C. E. could cause trouble, many spurious waves were thus obtained and these studies were therefore of little value. Glucose seemed in such experiments to give some waves as did methanol, formaldehyde, and acetaldehyde. The work on these compounds needs to be repeated before any definite statements are made, however, for the waves obtained, if due to the compound at all, were certainly badly distorted both by chloride interference and polarization.

Aniline, though undoubtedly influenced by these same factors, gave rather pronounced waves in 0.1N NaOH, and the evidence was such as to indicate that it would work well if proper precautions were taken. Similar evidences were noted even when HCl was used as the carrier, the wave apparently being strong enough to rise above the polarization (and possible contamination) effects.

The only compound studied with all known precautions was phenol. At the gold electrode in 0.1N NaOH, three waves were found, one of these appearing to be one of the spurious waves mentioned earlier. With platinum, when the electrode was depolarized by scraping, consistent and reproducible waves were obtained. Protection from air was necessary in most cases for, unless the solution was so protected, the wave height on successive runs decreased.

Studies on phenol at the platinum electrode and using the mercury-mercurous sulfate cathode were made in solutions of pH from 3.0 to 11.0. In each case the solutions were adjusted so they would have as nearly as

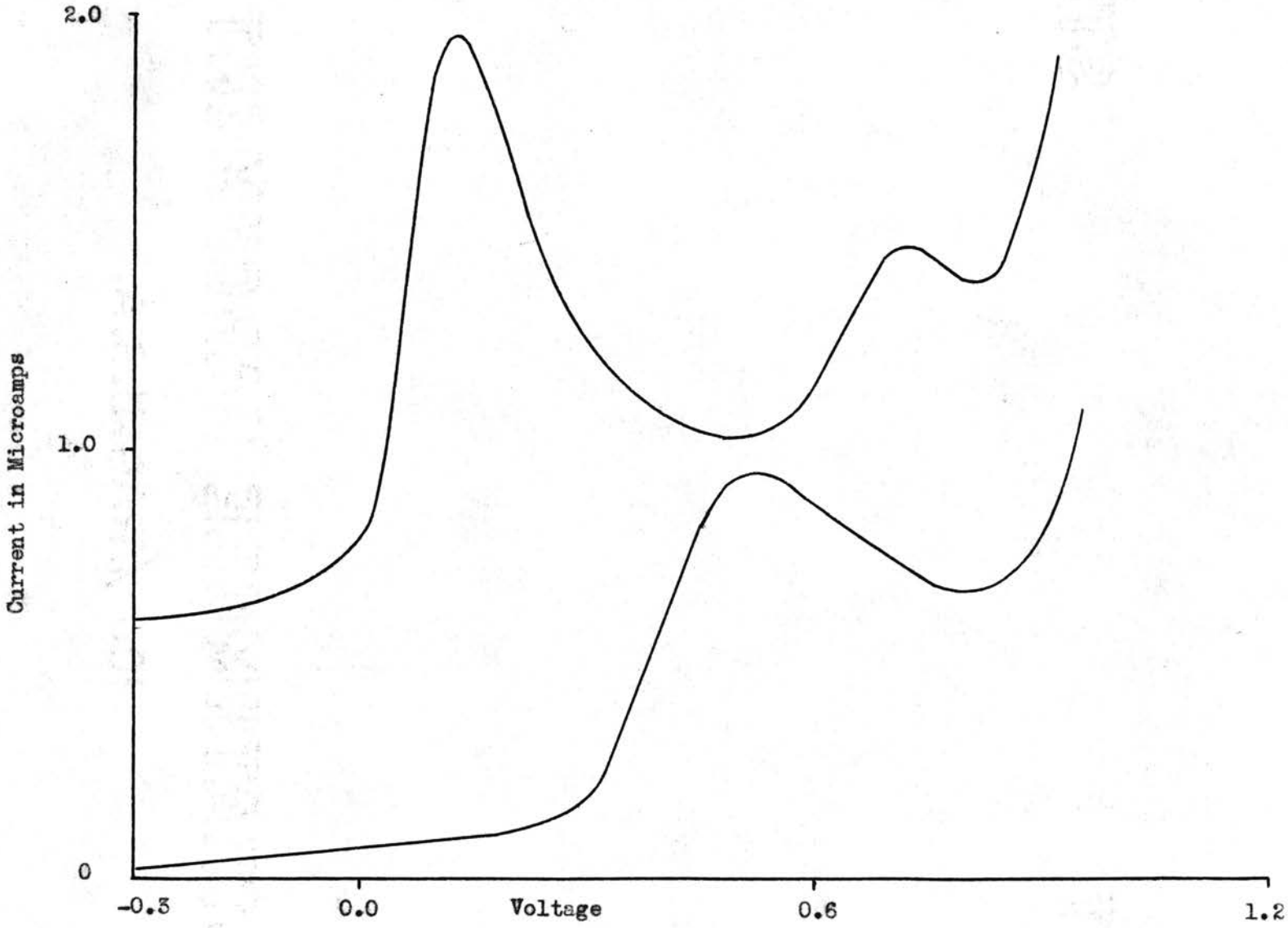

Figure 5

Phenol Waves, Scan Speed 10.5 Millivolts per Second
(Sat. $Hg|Hg_2SO_4$ Reference Electrode)

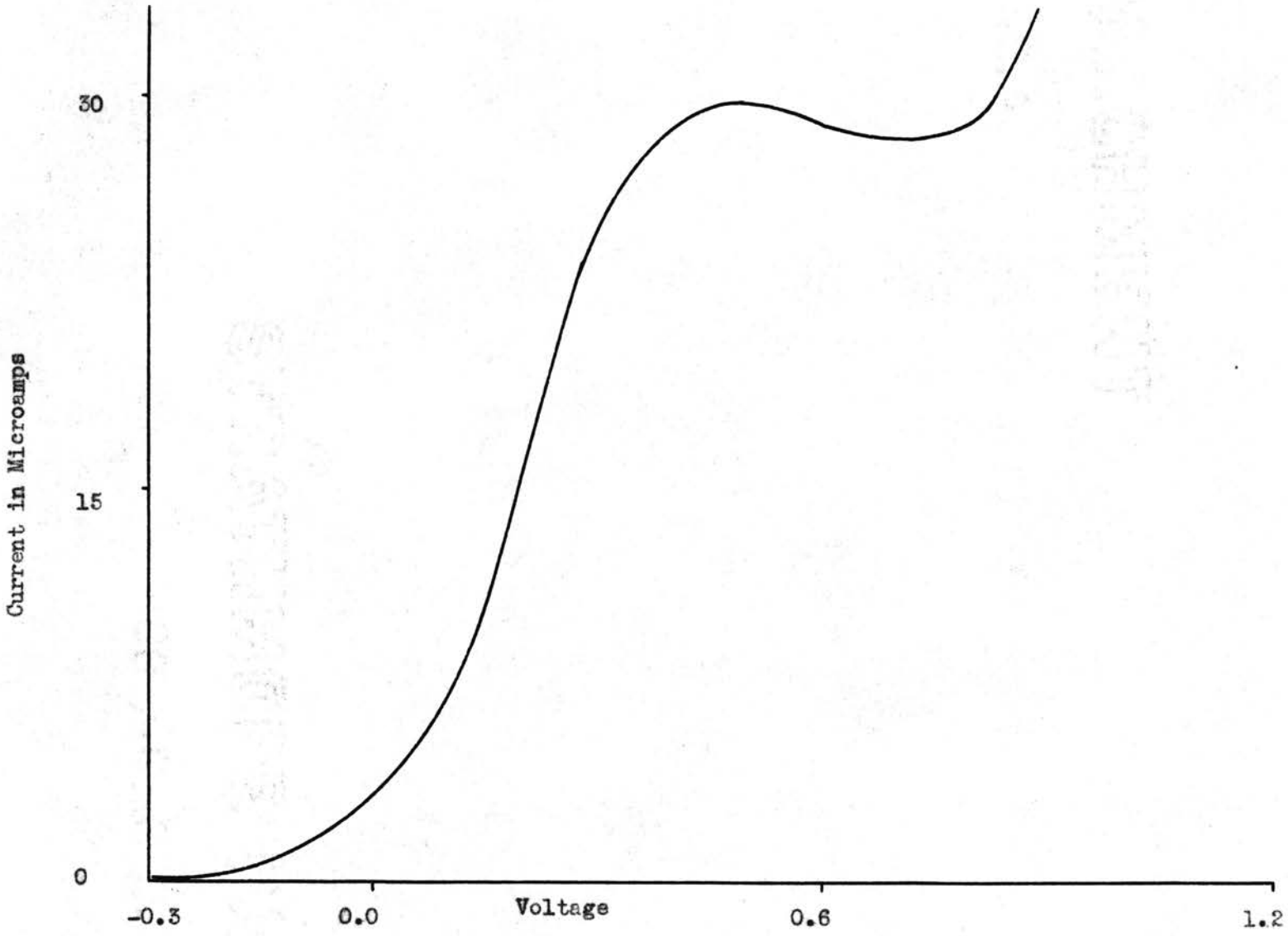

Figure 6

Phenol at pH 9.00, Scan Rate 100 Millivolts per Second
(Sat. $Hg|Hg_2SO_4$ Reference Electrode)

TABLE 2

Half-wave Potential of Phenol and Number of Microamps per Millimole with pH.

pH	$E_{1/2}$ vs. $Hg\|Hg_2SO_4$ Elect.	$E_{1/2}$ vs. S.C.E.	Conc.Phenol Moles/liter	I_d microamps	Microamps per Millimole
		Scan Rate 10.5 Millivolts per Second			
3.00	0.47	0.87	0.01	5.52	0.55
5.00	0.39	0.79	0.001	1.55	1.55
7.00	0.24	0.64	0.001	0.776	0.78
9.00	0.06	0.46	0.001	2.14	2.14
10.00	0.10	0.50	0.001	2.21	2.21
11.00	0.07	0.47	0.001	3.48	3.48
9.00	0.65*	1.05*	0.001	0.752	0.75
10.00	0.72*	1.12*	0.001	1.13	1.13
11.00	0.60*	1.00*	0.001	0.376	0.38
		Scan Rate 100 Millivolts per Second			
3.00	0.60	1.00	0.01	8.46	0.85
5.00	0.47	0.87	0.01	12.21	1.22
7.00	0.28	0.68	0.01	11.40	1.14
9.00	0.24	0.64	0.0011	5.96	5.96
10.00	0.24	0.64	0.01	10.34	1.03
11.00	0.17	0.57	0.01	12.45	1.25

*Second Wave

TABLE 3

Diffusion Current versus Concentration of Phenol

Carrier pH = 9.00

Concentration phenol solution added = 0.335M in pH 9.00 buffer solution

Run	ml Phenol Solution Added	Concentration Phenol Moles/l	$E_{1/2}$ vs. S.C.E.	I_d Microamps	Microamps per Millimole
		Scan Rate 10.5 Millivolts Per Second			
1	0	0		0	0
2	0.2	1.1×10^{-3}	0.47	1.86	1.69
3	1.0	5.5×10^{-3}	0.44	2.23	0.40
4	2.0	1.08×10^{-2}	0.44	3.06	0.28
5	8.0	3.94×10^{-2}	0.41	2.82	0.072
6	13.0	6.05×10^{-2}	0.40	3.29	0.054
		Scan Rate 100 Millivolts Per Second			
1	0	0		0	0
2	0.2	1.1×10^{-3}	0.64	5.96	5.42
3	1.0	5.5×10^{-3}	0.64	7.76	1.41
4	2.0	1.08×10^{-2}	0.62	8.23	0.758
5	8.0	3.94×10^{-2}	0.59	8.94	0.227
6	13.0	6.05×10^{-2}	0.59	9.40	0.155

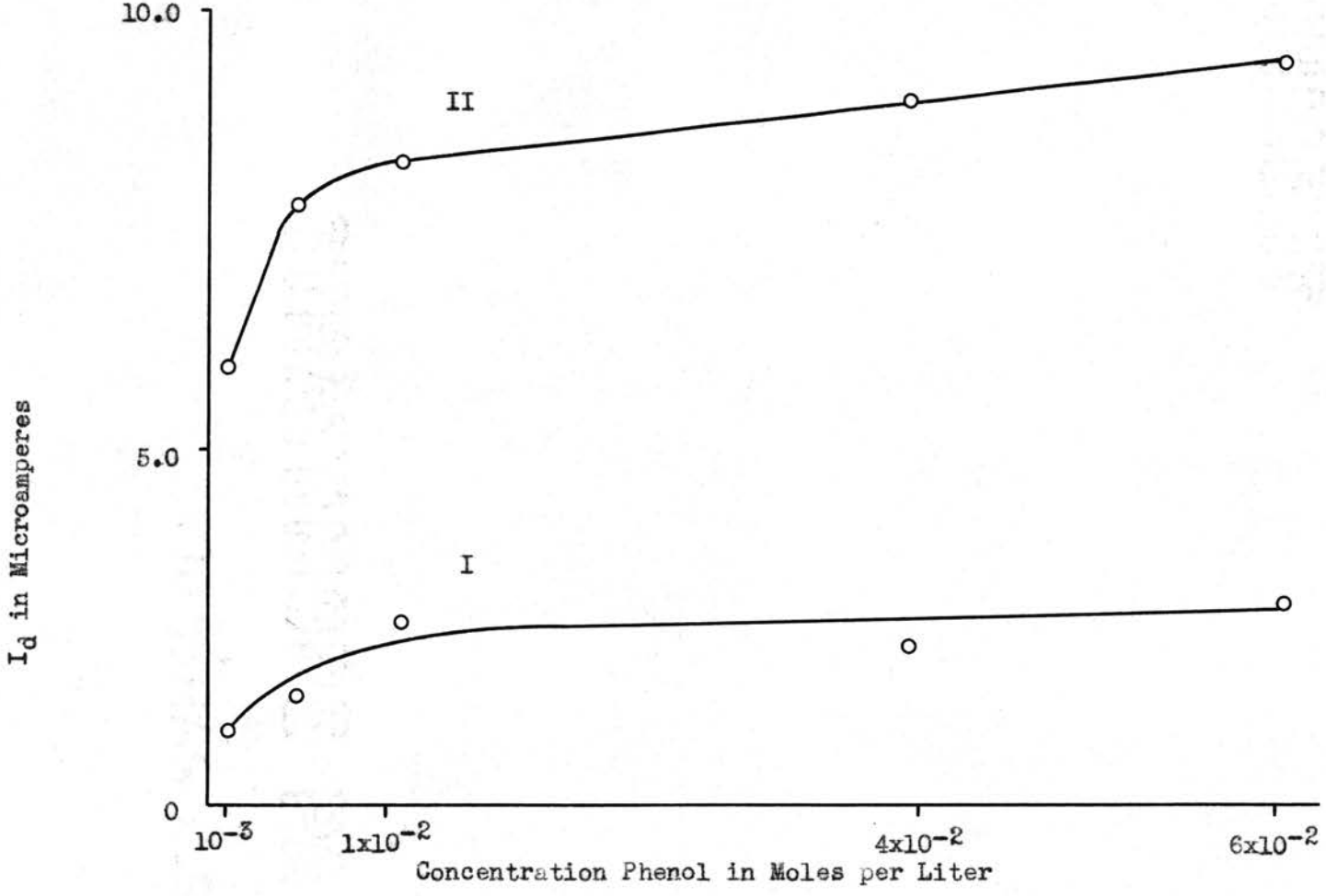

Figure 7

Graph of Diffusion Current (I_d) versus Concentration of Phenol
Curve I - Span Time 4'45"
Curve II - Span Time 30 seconds

possible the same ionic strength. In an effort to obtain some idea of the effect of polarization on the wave shape, runs were made at two speeds; i. e., scanning rates of 10.5 millivolts per second and 100 millivolts per second (a 3.0-volt span in 4 minutes 45 seconds and in 30 seconds, respectively). Figure 5 illustrates the types of waves formed at the lower span speed of 10.5 millivolts per second. As explained earlier, the sharp drop of the wave after the peak is reached is believed due to polarization. Figure 6 shows that this effect may be considerably reduced by making the runs at a higher speed, such as the 100 millivolt per second speed used in part of this research. The second wave noted in Curve II of Figure 5 was not found in any case when runs were made at high speeds, it being too close to the carrier wave to be seen even if it were present. Table 2 gives the data found on phenol at both scanning rates, including the half-wave potentials and the number of microamperes of current found per millimole of phenol present.

Phenol was tested to see if any regular relationship existed between diffusion current and concentration. Table 3 gives the data found, and Figure 7 gives the plot of I_d versus concentration. It is noteworthy that at higher concentrations the I_d does not change much with concentration changes. However, at concentrations of 5×10^{-3} and below, a more normal trend is seen. The increased polarization effects noted in the low-speed runs make this data less reliable than that of the 100 millivolt per second runs. The fast runs show that quantitative determinations of phenol could be made, but only at concentrations less than about 5×10^{-3}M and only at high scanning rates. All of these concentration curves were made at a pH of 9.0, in solutions made by adding from a burette a standard concentrated solution of phenol dissolved in the same buffer medium. The phenol solution was standardized by the bromine method recommended by Kolthoff and Stenger[17].

TABLE 4

Curve Characteristics of Polarization Wave on Carrier Curve

Following Hydrogen Depolarization*

i_d = 45.2 mm.

E vs. Sat'd. $Hg\|Hg_2SO_4$ E.	i mm.	$i_d - i$	$\frac{i}{i_d - i}$	log $i_d - i$	log $\frac{i}{i_d - i}$
.39	7.5	37.7	0.199	1.576	-0.701
.46	15.0	30.2	0.497	1.480	-0.304
.53	26.7	18.5	1.433	1.267	0.159
.56	32.7	12.5	2.615	1.097	0.417
.59	37.2	8.0	4.650	0.903	0.667
.63	41.0	5.2	7.88	0.716	0.897

*From a run made on a pH 7.0 buffer solution at a scanning rate of 100 millivolts per second.

TABLE 5

Data for Determination of Number of Electrons per Molecule in Phenol Reaction

pH 9.00 solution; phenol 10^{-2}M; scan rate 100 millivolts per second

i_d = 45.0 mm.

E vs. Sat'd. $Hg\|Hg_2SO_4$ E.	i mm.	i_d-i	$\frac{i}{i_d-i}$	log i_d-i	log $\frac{i}{i_d-i}$
0.15	13.5	31.5	0.428	1.498	-0.369
0.18	18.2	26.8	0.680	1.428	-0.167
0.23	31.2	13.8	2.26	1.140	0.354
0.26	36.0	9.0	4.00	0.954	0.602
0.29	40.0	5.0	8.00	0.699	0.903
0.31	42.5	2.5	17.00	0.398	1.231

pH 9.00 solution; phenol $1.1x10^{-3}$M; scan rate 100 millivolts per second

i_d = 63.0 mm.

0.21	23.5	39.5	.595	1.596	-0.226
0.24	30.5	32.5	.939	1.512	-0.027
0.28	38.0	25.0	1.52	1.398	0.182
0.31	45.0	18.0	2.50	1.255	0.398
0.34	50.0	13.0	3.84	1.114	0.584
0.38	56.0	7.0	8.00	0.844	0.903
0.41	59.0	4.0	14.75	0.602	1.169

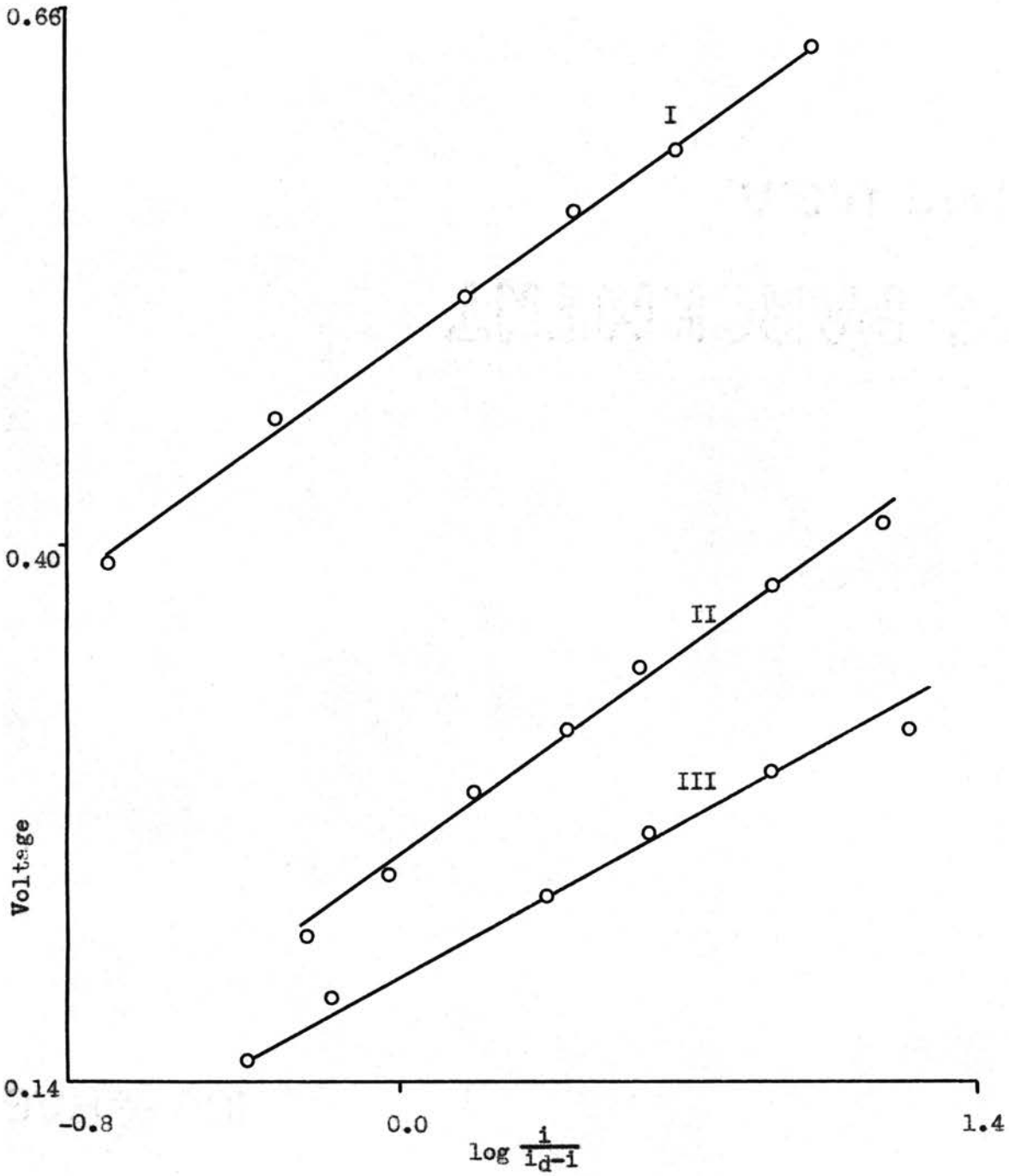

Figure 8

Graph E vs. log $\frac{i}{i_d - i}$ for Phenol and Polarization Waves

I - Polarization Wave

II - Phenol 10^{-3}M

III - Phenol 10^{-2}M

According to Kolthoff and Lingane[15], when a substance which is soluble in both its oxidized and its reduced form is determined at either the D. M. E. or a solid platinum microelectrode, the latter acts as a noble metal electrode and, if the reaction is rapid and reversible, the curve follows the equation:

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i}$$

From this the slope of a line obtained by plotting $E_{d.e.}$ vs. $\log \frac{i}{i_d - i}$ should be equal to 0.0591 ÷ n where n is the number of electrons per molecule involved in the electrode reaction. A similar equation for the reversible reduction of a cation to the metallic state, where the metal is insoluble in mercury or is being deposited on a solid microelectrode and where the deposited metal is in its most stable state requires that $E_{d.e.}$ be plotted against $\log (i_d - i)$ to give a slope equal to 0.0591÷ n. Although evidence acquired during these studies indicated that the polarization reaction occurring at the platinum electrode was neither rapid nor (probably) reversible, both of these graphical methods were applied to the polarization curve (as obtained in the phosphate buffer of pH 7 as carrier, after depolarization by hydrogen evolution) in an effort to determine the number of electrons involved. The same curves were likewise plotted for phenol although it seemed probable that the over-all oxidation of phenol would not be reversible.

The plot of E versus $\log \frac{i}{i_{d-i}}$ in all three cases used gave straight lines (see Figure 8 and Tables 4 and 5). Phenol was plotted at concentrations of 10^{-2}M and 1.1×10^{-3}M, in order to investigate the differences in these curves when the apparent polarization during the run was found to be low or high. From the plot of I_d versus concentration it appears that the polarization effect is considerably larger at 10^{-2}M. The slopes obtained in this plot of E versus $\log \frac{i}{i_{d-i}}$ gave no useful information on the reaction taking place at the platinum electrode. Theoretically a one-electron change has a

slope of 0.06, a two-electron change a slope of 0.030, and so forth. The values found for the polarization wave and for the 10^{-2}M and 10^{-3}M phenol waves were 0.14, 0.11, and 0.14 respectively.

Using the same data (see Tables 4 and 5), a plot of E versus log i_d-i was made (Figure 9). In all three cases the graphs obtained were curves, with no recognizable, meaningful slope.

One of the most interesting things noted in this research was that consistently better results, both in wave form and in variation of observed diffusion current with concentration, were obtained when the runs were made at high scanning rates and on solutions of low concentration. This evidence favors the hypothesis that products forming on the surface of the electrode and rendering part of it ineffective are responsible for the "dips" observed in the waves and the decreasing wave heights observed when repeated runs are attempted without depolarization. The current in polarography is a function of concentration; consequently, at low concentrations, smaller electrolysis currents flow. Slow scanning rates mean that greater time elapses during the making of a single run. From Faraday's law it is known that the quantity of product formed at an electrode (in this case presumably the polarization product as well as other products) is proportional to both time and current; consequently, if the theory of polarization postulated is correct, a decrease in either concentration or scanning time should have the effects observed.

Salicylic acid - This phenol was run at a pH of 10.0 in a phosphate buffer solution. The electrode was depolarized by scraping, but no wave was found even at concentrations of 0.01M. It would seem, therefore, that the compound is not oxidized below the potential of the carrier wave under the conditions of the experiment.

4-Hydroxybenzoic acid - This compound was run at a concentration of

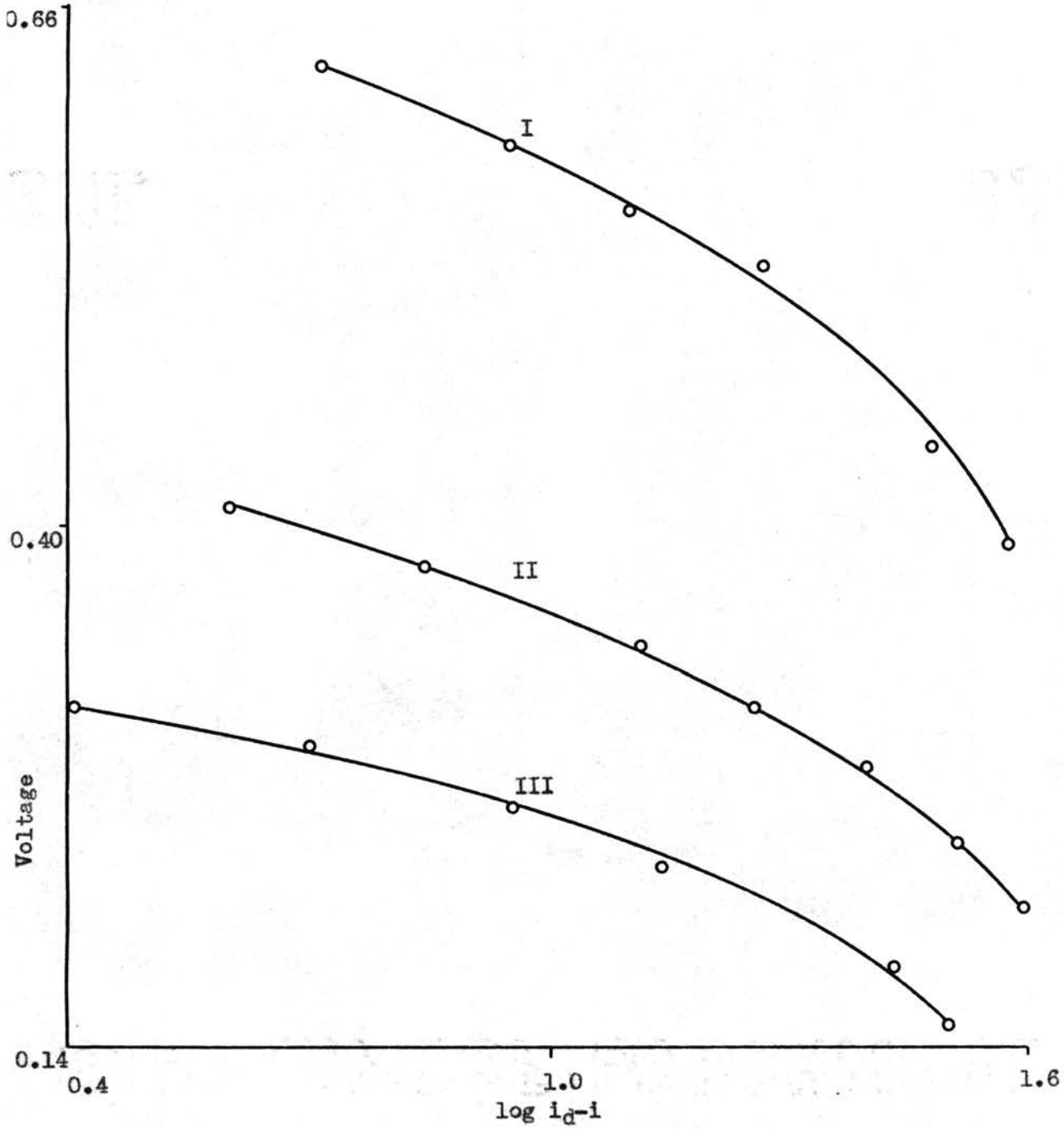

Figure 9

Graph of E vs. log i_d-i (Reference Electrode Sat. $Hg|Hg_2SO_4$)

I - Polarization Wave

II - Phenol 10^{-3}M

III - Phenol 10^{-2}M

0.01M in a pH 10.0 phosphate buffer solution. No wave was found.

4-Hydroxyisophthalic acid - This compound was run at a concentration of 0.005M, in a pH 10.0 buffer solution, this concentration being the limit of the solubility of the compound in this buffer solution. Again no wave was found, the phenol apparently being too difficult to oxidize at the potentials afforded by this carrier solution.

CONCLUSIONS

In view of the research presented in this paper, it is obvious that using these techniques, it should be possible to analyze many of the more easily oxidizable organic compounds at the platinum electrode using automatically recording polarographs of high scanning rates. In the case of phenol, it has been shown that this compound gives a reproducible wave at the rotating platinum electrode and that, over limited concentration ranges, the diffusion current is roughly proportional to concentration. It has also been shown that better current-voltage curves may be obtained by decreasing the length of time of a determination or (within limits) the concentration, thereby decreasing the effects of the polarization taking place at the electrode.

Other compounds investigated in a preliminary manner, and which appear to have good possibilities for further study, include aniline, formaldehyde, acetaldehyde, and glucose. The exploratory studies on these compounds indicate that they should, with proper technique, give good polarographic waves at the anode.

There are two principal limitations to the method as seen at this time. The major problem is still the one of depolarization of the electrode between runs. The method of scraping the electrode is adequate for research purposes, but is unduly tedious, and unless done very carefully, does not give a reproducible surface for each run. Further work should be done to determine the cause of this phenomenon and if possible, to develop a universally applicable technique for the prevention or removal of these effects. The second problem to be solved is the problem of a carrier electrolyte-solvent combination which will allow the positive potential to be increased past the point now possible using these buffer solutions. This may not be possible, but it is a worthy subject for further work. Extending the range of the carrier

electrolyte-solvent would greatly increase the number of compounds which could be oxidized, and thusly increase the usefulness of the method. Substances such as the other phenolic compounds tested in this research might then be oxidized, and the general value of anodic polarography greatly enhanced.

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BIOGRAPHY

Oscar C. Bridgeman, Jr., was born in Cambridge, Massachusetts, on August 28, 1925. He completed grade school at Palm Springs, California, and attended high schools in Washington, D. C., Oakland, California, and Berkeley, California, where he was graduated in 1943.

From 1943 until 1946 he served as a aerial navigator with the U. S. Army Air Force. He left the service as a 2nd. Lieutenant.

In the fall of 1946 he entered Harvard College, Cambridge, Massachusetts, and in June of 1950 he received the A. B. degree in chemistry. In the fall of 1950 the author came to Oklahoma A. and M. College to do graduate study in chemistry, where he has remained to this time.

The author married Patricia Ann Scott of Springfield, Massachusetts in December of 1947, and their son, David, was born in Stillwater, Oklahoma, in November of 1950.

TYPIST PAGE

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